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Vitrinite equivalent reflectance of Silurian black shales from the Holy Cross Mountains, Poland

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Abstract. A number of independent methods have been used to measure the thermal maturity of Silurian rocks from the Holy Cross Mountains in Poland. Black shales are characterized by diverse TOC values varying from 0.24-7.85%. Having calculated vitrinite equivalent reflectance using three different formulas, we propose that the most applicable values for the Silurian rocks are those based on Schmidt et al. (2015) equation. Based on this formula, the values range from % 0.71 $VR_{eqv}VLR$ (the vitrinite equivalent reflectance of the vitrinite-like macerals) to % 1.96 $VR_{eqv}VLR$. Alternative, complementary methods including Rock Eval pyrolysis and parameters based on organic compounds (CPI, Pr/*n*-C_{17}, Ph/*n*-C_{18}, MPI1, and MDR) from extracts did not prove adequate as universal thermal maturity indicators. We have confirmed previous suggestions that Llandovery shales are the most likely Silurian source rocks for the generation of hydrocarbons in the HCM.

Key-words: Holy Cross Mountains, Lower Silurian, maturation, graptolite reflectance, black shales

1. Introduction

One of the main methods used to measure the thermal maturation of sedimentary rock sequences is vitrinite reflectance (Hunt 1996). This method is especially applied to coals of different rank, from lignites to meta-antracites. Vitrinite reflectance is also commonly used in determining the maturity of dispersed organic matter. However, the method can only be applied to organic matter which occurs in sedimentary rocks younger than Upper Silurian. The reason for this limitation is related to the paucity of higher land plants before the Devonian. Measurement of the maturation of Silurian- and older sedimentary rocks is however possible using macerals other than vitrinite. Zooclasts (graptolites, chitinozoans, and scolecodonts) and other organic participles (e.g. solid bitumen) have been successfully used as equivalents of vitrinite in Lower Paleozoic rocks (e.g. Poprawa 2010; Petersen et al. 2013; Suárez-Ruiz et al. 2012). Both graptolites, and vitrinite-like particles in Lower Palaeozoic shales deemed to be graptolites by Petersen et al. (2013), are common in Silurian black shales; these particles yield well-defined reflectance populations and can be recommended as substitute of vitrinite grains in Lower Palaeozoic strata (Petersen et al. 2013).

Here, the complex characteristics of the thermal maturation of the Lower Silurian graptolite shales from the Holy Cross Mountains (HCM) are presented for the first time. The main method used was vitrinite equivalent reflectance measured on graptolite rhabdosomes, supported by Rock-Eval analysis and GC-MS measurement of organic compounds. Using this method could help to compare maturity results from the Silurian of the HCM with other regions of Poland where reflectance data are common (e.g. Poprawa 2010). The hydrocarbon potential of Llandovery to Wenlock black shales from the Kielce and Łysogóry region of the HCM is also assessed.

2. Current state of knowledge on maturation pattern of Palaeozoic sedimentary rocks in the HCM

Thermal maturation assessments of sedimentary rocks from the HCM have been performed using various methods including CAI, the colour-alteration index method (Belka 1990; Narkiewicz 2002; Narkiewicz, Malec 2006), the thermal alteration of acritarchs – TAI (Szczepanik 1997, 2001, 2007; Malec 2000; Stępień-Sałek 2011), Rock Eval pyrolysis (Malec et al. 2010; Joachimski et al. 2001; Marynowski et al. 2007, 2010; Marynowski, Filipiak 2007), vitrinite reflectance (Marynowski 1999; Marynowski et al. 2001, 2002; Wolkenstein et al. 2008; Marynowski, Simoneit 2009), organic-compound distribution (Marynowski 1999; Marynowski et al. 2001, 2002) and clay mineral data (Środoń, Trela 2012). In addition, 1-D burial-thermal numerical modelling studies based on published results have been performed (Poprawa et al. 2005; Narkiewicz et al. 2006, 2010).

The thermal maturity of the Cambrian rocks in the Kielce Region, separated from the highly mature Łysogóry region by the Holy Cross Fault, can be estimated as low to moderate (Szczepanik 1997, 2007). It is worth noting, however, that all results from the Cambrian rocks of the Łysogóry region, including those from the Pieprzowe Mts (e.g. Kamień Plebański well) relate to locations situated close to the HCF (Szczepanik 1997, 2001, 2007). In the Kielce region, thermal maturation also clearly increases towards the

fault (Zaręby 2 and Ublinek wells; see Szczepanik 1997). A similar thermal pattern has been reported for Ordovician sedimentary rocks, but data are few (Szczepanik 2007; Stępień-Sałek 2011). With regard to the Silurian sedimentary rocks, it is again obvious (especially for the western- and central part of Kielce region) that maturity ranges increase towards the HCF (Szczepanik 2007; Narkiewicz 2002) even if differences between the northern- and southern parts of the Łysogóry region are not so significant (Szczepanik 2007). Malec (2000) analyzed the coloration of microspores and acritarchs in the Upper Silurian greywackes of the HCM and observed, as had Szczepanik (1997) for the Cambrian, significant differences between the Kielce and Łysogóry regions. However, in the NW part of the Kielce region, he found organic matter to be highly altered and concluded that the thermal history of NW part of the Kielce region was similar to that of the Łysogóry region (Malec 2000).

This last conclusion was later supported by subsidence analysis and tectonic recostruction by Narkiewicz (2002). According to Narkiewicz (2002), the juxtaposition of the and the Łysogóry Block occurred due to right-lateral strike-slip after late Ludlowian- and before Emsian times. Based on the distinct similarities of the greywacke geochemical parameters from both regions, the consistent ages of detrital muscovite and facial observations, Kozłowski et al. (2014) doubted the previous interpretations; the similarities of the greywackes from both HCM regions indicate a common source and suggest that juxtaposition of the Łysogóry Block and Małopolska Massif must have been earlier.

Due to extensive study, partially connected with the many active- and inactive quarries and exposures in the HCM, knowledge about the thermal maturation of Devonian sequences (especially Middle- and Upper Devonian) is even more advanced than is the case with the older strata there. The first report concerning the degree of thermal maturation of Devonian organic material from the HCM based on the CAI (conodont Colour Alteration Index) method was that of Belka (1990). He showed increasing heat towards the HCF and concluded that the Devonian sedimentary rocks reached their maximum temperatures before the Permian when heat flow was much greater than in more recent times. Marynowski (1999), using vitrinite reflectance and biomarker data, concluded that thermal maturity of the Devonian-Carboniferous organic matter was achieved prior to the Late Carboniferous Variscan uplift. Narkiewicz et al. (2010) support this interpretation, concluding that maximum temperatures were reached before the Late Carboniferous uplift because of elevated Variscan heat flow and/or increased Carboniferous sediment thickness. Poprawa et al. (2005), in an alternative model, saw thermal maturity of the Variscan- and Permian-Jurassic successions as achieved during late Jurassic- or late Cretaceous burial with heat-flow equal to that of the present-day. However, the relatively low and narrow range values of calculated- and measured vitrinite reflectance for Middle Triassic (~ 0.6%; Marynowski et al. 2002), Lower Jurassic (0.47-0.59%; Marynowski, Simoneit 2009) and Upper Jurassic rocks (0.55-0.6%; Wolkenstein et al. 2008) throughout the HCM cast doubt on such a model (see also Narkiewicz et al. 2010). Recently, Środoń and Trela (2012) determined Variscan ages for maximum paleotemperatures in the Ostrówka and Bukowa Góra tuffites, but younger, early Jurassic-late Triassic ages for the Kowala tuffite suggest a significant Mesozoic diagenetic episode in the southern part of the Kielce region.

3. Samples

For this research, 34 graptolite shales and 2 concretions from 11 boreholes and 3 outcrops were sampled (Fig. 1). They various boreholes sampled were Daromin 1 (Dar 184.5, Dar 91.2, Dar 192.5, Dar 194.6, Dar 195.1), Dębniak (Deb 67.2), Jeleniów 2 (Jel 89.1, Jel 91.5), Kleczanów 1 (Kle 141, Kle 185, Kle 194, Kle 226.5), Lenarczyce 1 (Len 25), Mójcza 1 (Moj 11, Moj 33.5,), Szumsko Kol.2 (Szum 20), Wilków 1 (W 561, W 579.8), Zagórze 1 (Zag 75.2, Zag 87, Zag 88.2), Zarobiny 1 (Zar 158) and Zbrza 1 (Zb 10.9, Zb 11.1, Zb 11.3, Zb 11.5). Bardo Stawy (Bardo Staw 6P, Bardo Staw 9P), Bardo Prągowiec (Bardo con) and Mójcza (Moj con) were the three outcrops sampled. Detailed information about the ages of the black shales is shown in Table 1. Almost all of the samples were graptolite-rich shales, the exceptions being 4 samples from Bardo Stawy (chert sample from the O/S boundary) and samples from the wells Jeleniów 2 (89.1 m) and Kleczanów 1 (141 m and 185 m) in which zooclast particles were not found.

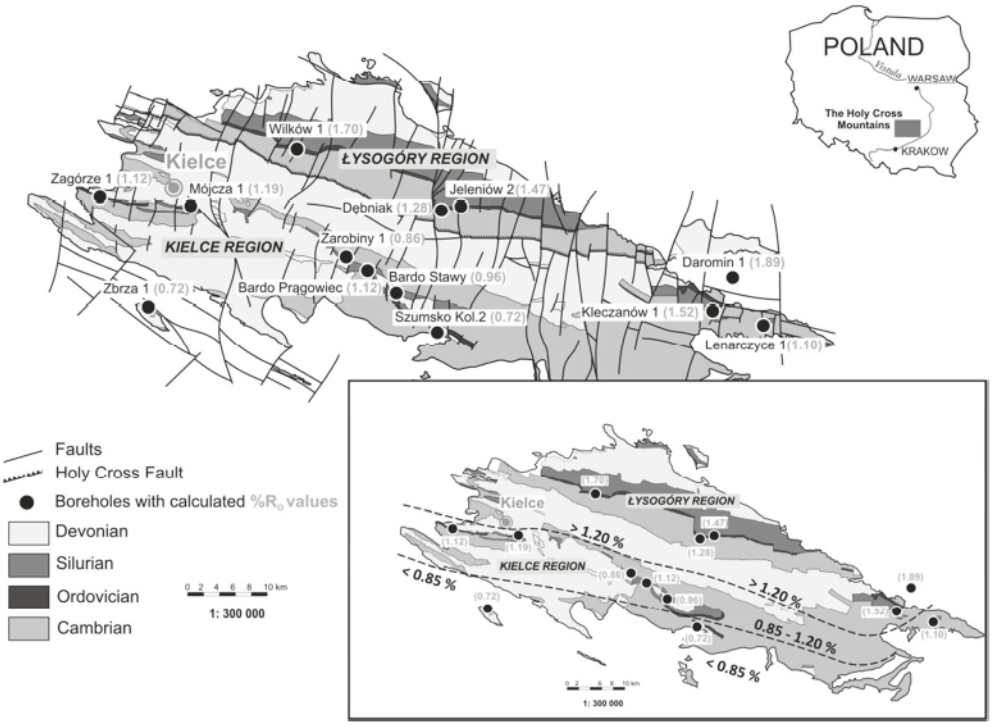

Fig. 1. Schematic geological map of the HCM showing the location of boreholes with values of vitrinite equivalent reflectance (%R_o) for Silurian shales

TABLE 1

Results of TOC (total organic carbon), TS (total sulphur), vitrinite equivalent reflectance and Rock-Eval analyses, in increasing %VR_{eqv}VLR order.
% R_{grap}(Av.) - % reflectance measured on graptolites, average for 50 measurements
% VR_{eqv} = 0.73 R(grap + vitr) + 0.16
R(grap + vitr) = % R_{grap}(Av.)
$T_{max(grap)}$ = 45.48 R(grap + vitr) + 400.16
$VLMR_o$ < 0,75%: VR_o% =1.26 $VLMR_o$ +0.21;
$VLMR_o$ = 0,75 - 1.50%: VR_o% =0,28 $VLMR_o$ +1.03;
VLR ≤ 0.75%: VR_{eq}VLR = 0.9916VLR + 0.1590;
VLR > 0.75% & ≤ 1.50%: VR_{eq}VLR = 0.9046VLR + 0.3786
(1) Petersen et al. (2013), (2) Xianming et al. (2000), (3) Schmidt et al. (2015).

Sample	Age	TOC	$TOC_{(R-E)}$	TS	% $R_{grap(Av.)}$	% VR_{eqv} (1)	% VR_o (2)	% VR_{eqv} VLR (3)	$T_{max(grap)}$	T_{max}	S_1	S_2	HI	OI
		[%]	[%]	[%]					°C	°C	mgHC/g rock		mgHC/gTOC	$mgCO_2$/g TOC
Zb 10.9	Llandovery	5.92	nd	2.07	0.56	0.57	0.91	0.71	425.89	nd	nd	nd	nd	nd
Szum 20	Llandovery	7.85	8.30	1.01	0.57	0.57	0.92	0.72	426.26	429	1.73	32.52	392	10
Zb 11.1	Llandovery	nd	6.02	nd	0.58	0.58	0.93	0.73	nd	431	0.70	25.54	424	3
Bardo Staw 6P	Llandovery	nd	nd	nd	0.70	0.67	1.09	0.85	430.59	nd	nd	nd	nd	nd
Zar 158	Wenlock	1.13	nd	1.20	0.70	0.67	1.10	0.86	430.83	nd	nd	nd	nd	nd
Bardo Staw_9P	Llandovery	nd	nd	nd	0.76	0.71	1.24	1.06	432.58	nd	nd	nd	nd	nd
Zag 75.2	Wenlock?	1.29	nd	1.15	0.77	0.73	1.25	1.08	433.16	nd	nd	nd	nd	nd
Len 25	Wenlock?	1.40	1.73	0.01	0.79	0.74	1.25	1.10	433.74	438	0.09	1.43	83	74
Zag 88.2	Wenlock	1.15	nd	0.83	0.82	0.76	1.26	1.12	434.62	nd	nd	nd	nd	nd
Bardo con	Low.Ludlowian	0.24	nd	0.35	0.82	0.76	1.26	1.12	434.68	nd	nd	nd	nd	nd
Moj 11	Wenlock	1.39	0.96	0.84	0.85	0.78	1.27	1.15	435.57	440	0.25	2.68	280	9
Zag 87	Wenlock	1.58	nd	0.83	0.87	0.80	1.27	1.17	436.48	nd	nd	nd	nd	nd

Moj 33.5	Wenlock	1.31	nd	0.56	0.95	0.85	1.30	1.24	438.89	nd	nd	nd	nd	nd
Deb 67.2	Wenlock	3.83	nd	2.41	1.00	0.89	1.31	1.28	440.58	nd	nd	nd	nd	nd
Moj con	Wenlock	0.32	nd	0.00	1.01	0.90	1.31	1.29	440.88	nd	nd	nd	nd	nd
Jel 91.5	Wenlock	1.45	1.17	1.14	1.20	1.04	1.37	1.47	447.40	331*	0.05	0.09	8	8
Kle 226.5	Wenlock	2.14	1.72	0.73	1.25	1.07	1.38	1.51	448.83	440	0.54	4.23	246	4
Kle 194	Wenlock	1.13	0.83	1.17	1.28	1.10	1.39	1.54	450.02	440	0.24	1.45	175	10
W 561	Llandovery	1.46	1.13	1.21	1.43	1.20	1.43	1.67	454.93	343*	0.04	0.09	8	11
W 579.8	Llandovery	2.20	1.91	1.38	1.50	1.25	1.45	1.73	457.12	306*	0.14	0.16	9	9
Dar 195.1	Wenlock	2.25	nd	1.99	1.60	1.33	1.48	1.83	460.65	315*	0.01	0.03	52	233
Dar 194.6	Wenlock	2.13	2.44	1.99	1.74	1.43	1.52	1.96	465.35	322*	0.12	0.14	6	10
Dar 184.5	Wenlock	nd	1.20	nd	nd	nd	nd	nd	nd	422	0.06	0.11	9	12
Dar 91.2	Wenlock	nd	2.37	nd	nd	nd	nd	nd	nd	295*	0.09	0.07	3	8
Dar 192.5	Wenlock	nd	1.89	nd	nd	nd	nd	nd	nd	331*	0.06	0.08	4	11
Jel 89.1	Wenlock	nd	1.54	nd	nd	nd	nd	nd	nd	608	0.03	0.10	7	6
Kle 141	Wenlock	nd	0.21	nd	nd	nd	nd	nd	nd	436	0.04	0.21	100	20
Kle 185	Wenlock	nd	0.76	nd	nd	nd	nd	nd	nd	438	0.23	1.20	157	15
Zb 11.3	Llandovery	nd	5.28	nd	nd	nd	nd	nd	nd	433	0.54	21.62	409	3
Zb 11.5	Llandovery	nd	8.49	nd	nd	nd	nd	nd	nd	439	0.83	37.43	441	4

*invalid data because of too high thermal maturity of organic matter or too low TOC content
nd - no data

4. Methods

4.1. Graptolite reflectance

Petrographic analyses were carried out on pellets of all samples prepared according to procedures described in PN-ISO 7404-2:2005. An optical Axio Imager A2m microscope was used at magnification x500. Random reflectance (Rr) was measured on samples containing organic matter visible under the microscope. The measurements were taken according to PN-ISO 7404-5:2002 at 50 points depending on the level of alteration of the organic matter using sapphire standards of the value 0.42%, 0.898% and 1.42% reflectance.

4.2. Total organic carbon (TOC) and total sulphur (TS)

Total carbon (TC), total inorganic carbon (TIC) and total sulphur (TS) contents were measured using an Eltra CS-500 IR-analyzer with a TIC module. TC was determined using an infrared cell detector on CO_2 gas evolved by combustion under an oxygen atmosphere. TIC contents were derived by reaction with 15% hydrochloric acid and CO_2 was determined by infrared detector. TOC was calculated as the difference between TC and TIC. Calibration was made using the Eltra standards. Analytical precision and accuracy were better than ±2% for TC and ±3% for TIC.

4.3. Rock-Eval

Total organic carbon was measured using the Rock Eval 6 Turbo apparatus. After washing with water and drying at room temperature, samples were crushed and powdered to a fraction of < 2 μm. Weights of the samples prepared for Rock Eval analysis ranged from 35-100 mg. Measurement proceeds in two cycles. In the first cycle, the sample was fed into a pyrolytic oven and then heated to 650°C in an atmosphere of helium was. Volatile hydrocarbons present were released at 350°C and their contents measured by the flame-ionization detector and expressed as a peak S_1. In a further phase of this cycle, thermal decomposition of the sample up to a temperature of 650°C causes the pyrolysis of kerogen and the release of hydrocarbons, carbon dioxide and carbon monoxide from the thermal decomposition of macromolecules. The results are presented as peak S_2. In the second cycle, a sample is put in an oxidative oven and heated to 850°C in an oxygen atmosphere. The heating causes the release of carbon dioxide and carbon monoxide from residual- and unproductive organic matter and from mineral matter. The T_{max} parameter represents the temperature of the maximum release of hydrocarbons from the cracking of kerogen during pyrolysis. Analysis were performed in the Polish Geological Institute / National Research Institute, Warsaw.

4.4. Extraction and separation

The crushed samples (to ca 100 mesh) were extracted using a dichloromethane (DCM) / methanol mixture (5:1 v:v) with an accelerated Dionex ASE 350 solvent extractor. Extracts were separated into aliphatic-, aromatic- and polar fractions by modified column

chromatography (Bastow et al. 2007). Silica-gel was first activated at 120°C for 24 h, cooled and poured into Pasteur pipettes. Three eluents were used for fraction collection, namely, *n*-pentane for the aliphatic fraction, *n*-pentane and DCM (7:3) for the aromatic fraction, and DCM and methanol (1:1) for the polar fraction). All solvents were spectroscopically pure and of super-dehydrated grade. In a blank sample (silica gel) analysed using the same procedure (including extraction and separation on columns), only trace amounts of phthalates were detected.

4.5. Gas chromatography – mass spectrometry (GC–MS)

The GC-MS analyses were carried out using an Agilent Technologies 7890A gas chromatograph and an Agilent 5975C Network mass spectrometer with a Triple-Axis Detector at the Faculty of Earth Sciences, Sosnowiec, Poland. Helium (6.0 Grade) was used as the carrier gas at a constant flow 2.6 ml/min. Separation was on either of two different fused silica columns:

(i) J&W HP5-MS (60 m x 0.32 mm i.d., 0.25 µm film thickness) coated with a chemically bonded phase (5% phenyl, 95% methylsiloxane). The GC oven temperature was programmed from 45°C (1 min) to 100°C at 20°C/min, then to 300°C (held for 60 min) at 3°C/min. Solvent delay = 10 min.

(ii) J&W DB35-MS (60 m x 0.25 mm i.d., 0.25 µm film thickness) coated with a chemically bonded phase (35% phenyl, 65% methylsiloxane). The GC oven temperature was programmed from 50°C (1 min) to 120°C at 20°C/min, then to 300°C (held for 60 min) at 3°C/min. Solvent delay = 15 min. The GC column outlet was connected directly to the ion source of the MSD. The GC–MS interface was at 280°C, while the ion source and the quadrupole analyzer were at 230 and 150°C, respectively. Spectra were recorded from *m/z* 45–550 (0–40 min) and *m/z* 50–700 (> 40 min). The mass spectrometer was operated in the electron impact mode (ionisation energy 70 eV).

4.6. Quantification and identification

An Agilent Technologies MSD ChemStation E.02.01.1177 and the Wiley Registry of Mass Spectral Data (9th edition) software were used for data collection and spectra processing.

5. Results

5.1. Differences in vitrinite equivalent reflectance and total organic carbon (TOC) values

The content of total organic carbon (TOC) and total sulphur (TS) was measured for 19 samples. Although macroscopically rather similar, the black shale samples are characterized by major variations in TOC (0.24 % − 7.85%) and total sulphur amounts ranging from ca 0% to 2.41% (Table 1). Despite of differences in organic carbon content, graptolite fragments were found in considerable amounts in almost all samples.

The graptolite reflectance measurements were carried out on 21 samples of Lower Silurian shales (Table 1, Fig. 2). The average of 50 measurements (% $R_{grap(Av.)}$) for every sample was calculated. Vitrinite equivalent reflectance values shown in Table 1 are based on three different formulas defined by Petersen et al. (2013), Xianming et al. (2000) and Schmidt et al. (2015) that are listed in Table 1. Significant differences in the results obtained (Table 1) prompted a critical review of the different equations (see Section 6.1 below).

Based on the graptolite-reflectance measurements, $T_{max(grap)}$ values were calculated (Table 1) according to the formula of Petersen et al. (2013). In general, the $T_{max(grap)}$ values confirm with those of T_{max} obtained using the Rock Eval method (Table 1).

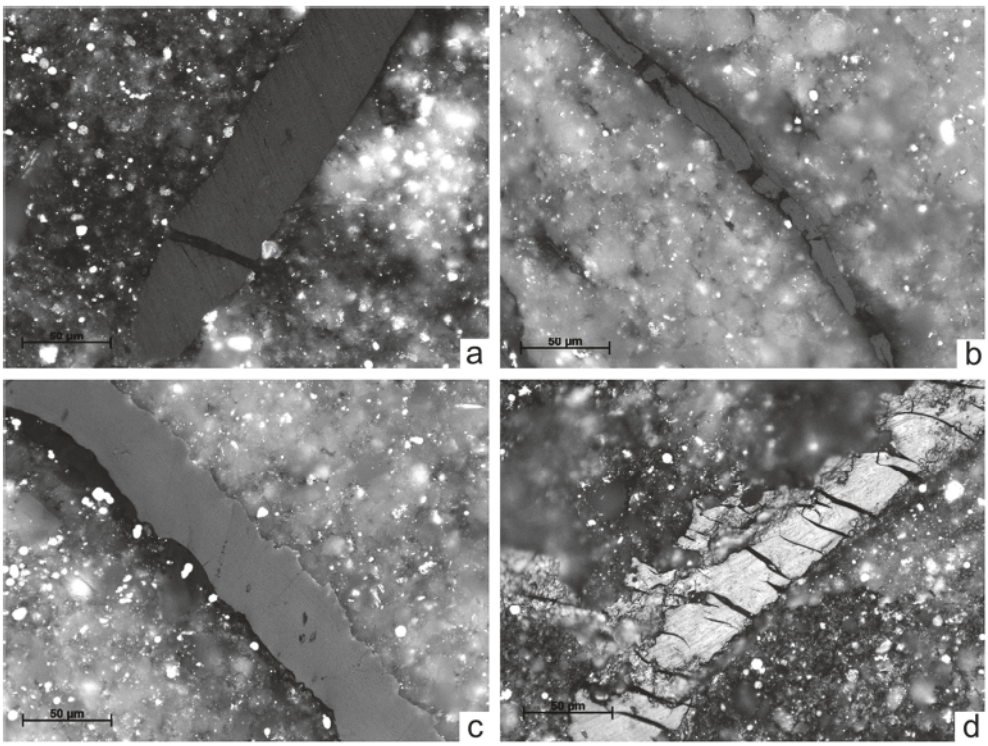

Fig. 2. Photomicrographs (white reflected light, oil immersion) of parts of graptolite rhabdosomes. Reflectance value increases from (a) to (d). (a) Llandovery shale, Zbrza PIG-1, HCM, Poland (sample Zb 10.9). (b) Wenlock shale, Zagórze IG-1, HCM, Poland (sample Zag 88.2). (c) Wenlock shale, Kleczanów PIG-1, HCM, Poland (sample Kle 194.0). (d) Wenlock shale, Daromin IG-1, HCM, Poland (sample Dar 194.6)

5.2. Rock Eval determination

The source-rock potential of the Lower Silurian shales was evaluated on the basis of 10 of 19 Rock Eval measurements. The samples from the Daromin-, Jeleniów- and Wilków

boreholes were not used because of the advanced thermal transformation of organic matter in the Łysogóry region.

The samples can be divided into four groups. The first group is composed of four samples from the Zbrza 1 and Szumsko Kol.2 wells. Their hydrogen index values (HI) range from 392-441 mg HC/g TOC and thermal maturity, as expressed by the T_{max} parameter, from 429-439°C, characteristic for type II kerogen (Fig. 3, 4). Values of S_2 range from 21.6 -37.4. The high HI index and T_{max} values combined with the high content of organic carbon (5.28-8.49%) are indicative of very good source rocks for hydrocarbon generation (Peters, Cassa 1994).

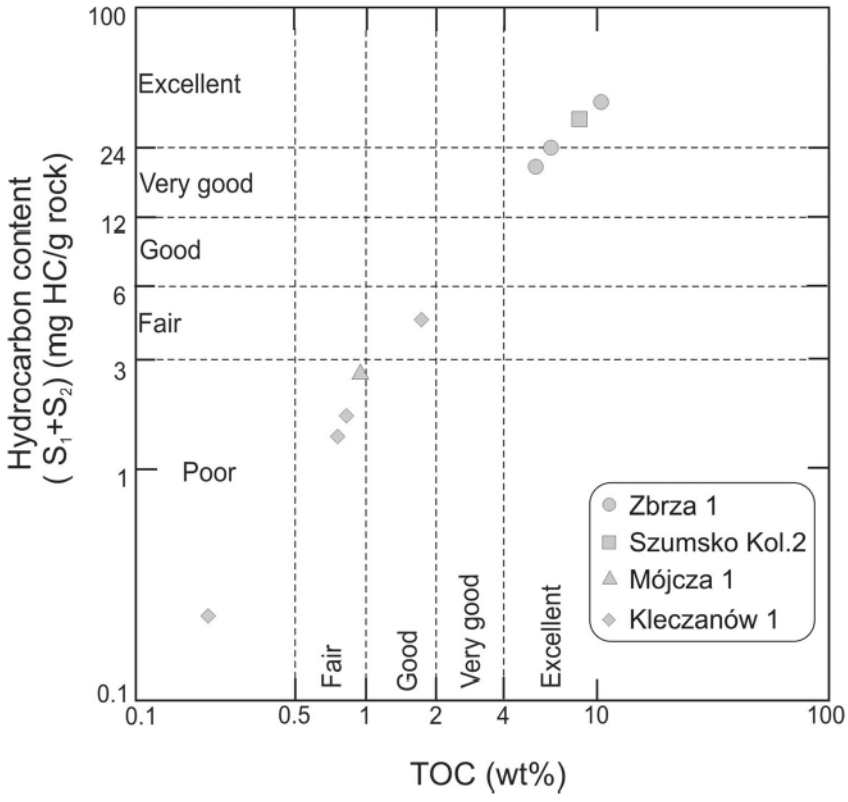

Fig. 3. Diagram of hydrocarbon content vs. total organic carbon showing the petroleum source rock potential of chosen Lower Silurian shales from the HCM

Samples in the second group (Mojcza 1 and Kielczanów 1 boreholes) are characterized by lower HI values between 157-280 mg HC/g TOC, T_{max} values between 438-440°C and S_2 values between 1.2-4.2 mg HC/g TOC (Fig. 3). TOC amounts varying from 0.76-1.72% indicate good- (Kle 226.5), fair- (Mojcza 1) and poor (Kle 185, Kle 194) source rock potential (Peters, Cassa 1994). Similarly to the Zbrza 1 and Szumsko Kol.2 wells (group 1), these samples contain type II kerogen (Fig. 4).

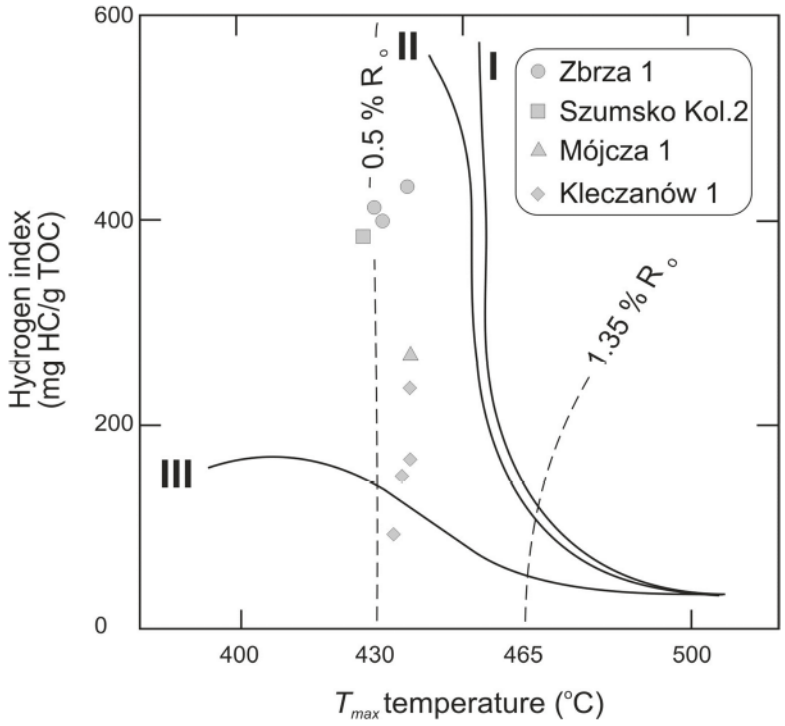

Fig 4. Diagram of the hydrogen index vs. T_{max} showing the kerogen type of chosen Lower Silurian shales from the HCM

The third group consists of two samples from the Lenarczyce 1 and Kleczanów 1 boreholes. Their values of petroleum potential are 83 and 100 HC/g TOC and T_{max} values are 438 and 436°C, respectively. There very low values of S_1 and generation potential S_2 (Table 1) suggest that the black shales from Lenarczyce 1 and Kleczanów 1 are not good source rocks (Peters, Cassa 1994). The sample from Lenarczyce 1 contains type II kerogen and that from Kleczanów 1 kerogen type III, most probably reflecting organic-matter deposition under oxic conditions.

The last group comprises samples from the Daromin 1, Jeleniów 2 and Wilków 1 boreholes. The hydrogen potential of these is very low (3-9 mg HC/ g TOC) and, in conjunction with low values of S_1 and S_2 and high degree of thermal transformation (see reflectance values in Table1), indicates that they contain overmature organic matter. For this reason, these samples are not discussed further as potential source rocks.

5.3. Molecular parameters and their use

Selected molecular parameters characterizing organic matter maturation from the Silurian shales are shown in Table 2. Indicators such as Carbon Preference Index (CPI), Pr/*n*-C_{17} and Ph/*n*-C_{18} were calculated based on *n*-alkanes and isoprenoid distribution. CPI values range from 0.7-1.1. For the first group of samples, %0.71 VR_{eqv} VLR - %1.29 VR_{eqv} VLR (the vitrinite equivalent reflectance of the vitrinite-like macerals), CPI values range

around 1.0-1.1, whereas for the second group of highly mature samples (%1.47 VR_{eqv} VLR - %1.96 VR_{eqv} VLR), they lie in the insignificantly lower range of 0.7-1.1. As to be expected, CPI values do not change with measured vitrinite equivalent reflectance, but show the same value, for example, for the sample of % 0.71 VR_{eqv} VLR as for that of much higher maturity of % 1.51 VR_{eqv} VLR. This is because the only organic-matter type in the Silurian black shales is marine type II kerogen, with no terrestrial input and no differences between concentrations of odd- vs. even *n*-alkanes. A similar situation pertains in the case of Pr/*n*-C_{17} and Ph/*n*-C_{18}; though the values should decrease with increasing vitrinite equivalent reflectance, no such correlation has been noted (Table 2).

Phenanthrene and methylphenanthrenes were identified in almost all black shales, usually as main constituents in the aromatic fraction. Based on their distribution, the methylphenanthrene index (MPI1), the methylphenanthrene ratio (MPR) and the calculated vitrinite reflectance from methylphenanthrene index (% R_c) were determined. The values of % R_c (0.04-1.42) are lower than the measured vitrinite equivalent reflectance (VR_{eqv} VLR) values. We do not endorse these parameters for use in the estimation of organic maturity in the Silurian black shales because (1) elevated concentrations of 9-MePh relative to other MePh isomers (Fig. 5), most probably connected with preferential geosynthesis of this compound (Alexander et al. 1995) and (2) the occurrence of marine kerogen type, when use of MPI is not recommended (Radke 1988).

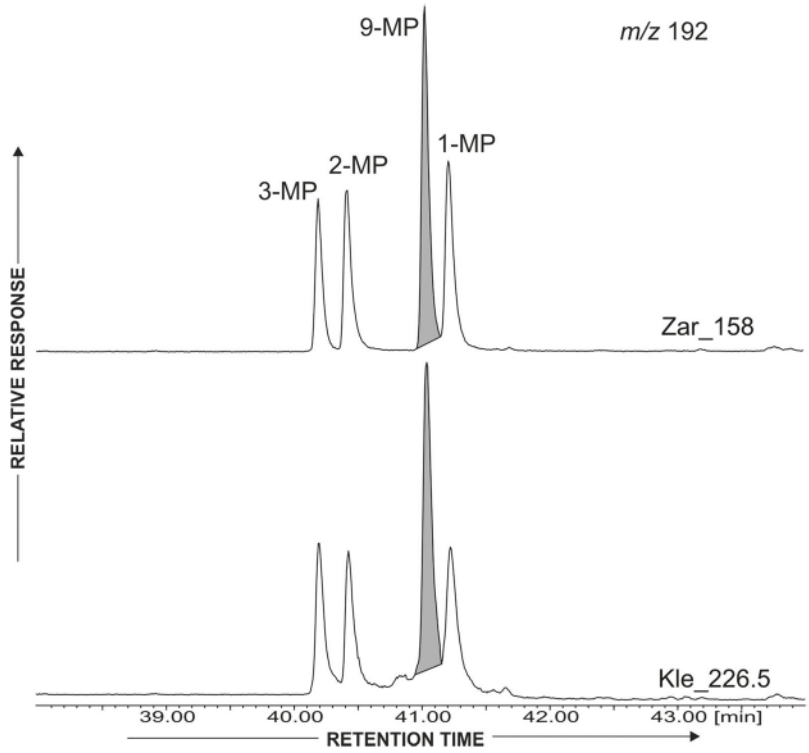

Fig. 5. Partial chromatogram (*m/z* 192) showing elevated relative concentration of 9-methylphenanthrene (shaded peak) in Silurian black shales from the HCM.

Dibenzothiophenes were another group of compounds used to determine thermal maturity. Methyldibenzothiophene ratio (MDR) values correlate with graptolite reflectance values, but because these compounds were detected in a few samples only due to the very low relative concentration of organic sulphur compounds in the Silurian black shales (Table 2), this parameter is of limited use as the maturity indicator in these shales. The same limitation applies in the case of hopane- and sterane biomarkers which are present as minor compounds only in shales of low maturity.

6. Discussion

6.1 Graptolite reflectance, maturity range and comparison with younger sediments

Values of measured graptolite reflectance calculated using three different formulas differ significantly (Table 1). The formula of Xianming et al. (2000) seems to be useless for our samples; the results are unrealistic and do not correlate with any other results. For example, the samples from the Zbrza 1 and Szumsko Kol.2 wells of evidently low maturity have calculated vitrinite reflectance values of ca 0.9% which seems impossible in the light of low T_{max} values (Table 1), TAI values of 1-2 (Szczepanik 2007) and the occurrence of relatively unstable biomarkers. The results based on the formula of Petersen et al. (2013) are more realistic (Table 1), but seem too low when compared to maturation data for younger sequences (e.g. Devonian sediments). For example, measured vitrinite reflectance from the Kowala and Radkowice quarries near the Zbrza 1 borehole range from 0.52-0.65% (Marynowski 1999; Rospondek et al. 2009) and calculated values of VR_{eqv} = 0.57% (Table 1). A value (R_{cs} = 0.65%) calculated from MDR for Middle Devonian limestones from Dębska Wola is higher than that calculated for Rhudanian black shales (Marynowski 1999). The fact that the thickness of rocks younger than Lower Silurian and older than Upper Devonian in the area reaches ca 1000 m (see Malec 2006; Romanek, Rup 1990) can explain a difference of ca 0.2-0.3% in vitrinite reflectance. As it seems that most correct values are those based on the Schmidt et al. (2015) equation, these values ranging from % 0.71 VR_{eqv}VLR in the Zbrza 1 borehole to % 1.96 VR_{eqv}VLR in the Daromin 1 borehole are here deemed appropriate for Silurian shales in the HCM. Generally, thermal maturation increases from S to N (Fig. 1) with the highest values applying to boreholes near the HCF. Due to lack of data, maturation values for the northernmost Silurian strata remain unknown.

Values of VR_{eqv}VLR from the Mójcza 1 well and outcrop concretion (Moj 11, Moj 33.5, Moj con) are consistent; they range from 1.15-1.29% (Table 1). However, CAI values for Ordovician conodonts from Mójcza 1 are very low (CAI=1; Belka 1990) and seem unlikely in the light of the Silurian results above, values of TAI = 2 (Szczepanik 2007) and relatively high reflectance values for nearby Devonian rocks (Marynowski 1999). An explanation of this discrepancy may be the lithology of the conodont-bearing, clay-free Ordovician limestones. Clay minerals play the important role in the catalytic conversion of organic matter (see e.g. Tannenbaum et al. 1986), and due to lack of clays in the Ordovician limestones from Mójcza 1, the colour of organic matter in conodonts does not significantly change. Clearly, the use of more than one method is to be recommended in thermal-range determination and thermal-history reconstruction.

TABLE 2

Geochemical characteristics of Silurian rocks samples from the HCM in increasing order of %VR_{eqv}VLR values (nd - no data; b.d. - below detection)

Sample	TOC [%]	% VR_{eqv} VLR (3)	CPI	Pr/*n*-C_{17}	Ph/*n*-C_{18}	MPI1	MPR	% R_c	MDR	% R_c(DBT)	T_{max}(DBT)
Szum 20	7.85	0.72	1.0	1.0	0.5	0.6	1.0	0.8	1.7	0.6	431.8
Zb 11.1	nd	0.73	1.1	2.6	0.8	0.45	0.73	0.67	b.d.	b.d.	b.d.
Zar 158	1.13	0.86	1.1	0.1	0.1	0.39	0.87	0.63	b.d.	b.d.	b.d.
Zag 75.2	1.29	1.08	1.0	0.9	0.7	0.50	0.97	0.70	5.46	0.91	450.84
Len 25	1.40	1.10	1.0	0.5	0.4	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Bardo con	0.24	1.12	1.0	1.9	1.3	0.37	0.44	0.62	b.d.	b.d.	b.d.
Zag 87	1.58	1.17	1.0	0.7	0.4	0.51	1.07	0.71	b.d.	b.d.	b.d.
Moj 33.5	1.31	1.24	1.0	0.7	0.3	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Moj con	0.32	1.29	1.0	0.8	0.5	0.3	0.8	0.6	b.d.	b.d.	b.d.
Jel 91.5	1.45	1.47	0.7	0.5	0.7	0.4	3.0	0.6	b.d.	b.d.	b.d.
Kle 226.5	2.14	1.51	1.1	0.4	0.2	0.5	0.7	0.7	9.6	1.2	472.0
W 561	1.46	1.67	0.8	0.5	0.5	0.9	2.1	0.9	b.d.	b.d.	b.d.
W 579.8	2.20	1.73	0.9	0.2	0.4	0.4	2.0	0.7	b.d.	b.d.	b.d.
Dar 195.1	2.25	1.83	0.9	0.9	0.8	0.7	1.7	0.8	b.d.	b.d.	b.d.
Dar 194.6	2.13	1.96	1.0	0.8	0.8	0.2	1.6	0.5	5.0	0.9	448.4
Kle 194	1.13	nd	1.1	0.4	0.3	0.6	0.9	0.8	20.4	2.0	527.2
Zb 11.3	nd	nd	1.1	2.1	0.7	0.54	0.88	0.72	b.d.	b.d.	b.d.
Zb 11.5	nd	nd	1.1	1.6	0.6	0.62	0.95	0.77	b.d.	b.d.	b.d.

Also requiring clarification is the high variability of maturation values between boreholes in the eastern part of the HCM (Fig. 1). For the adjacent Lenarczyce 1, Kleczanów 1 and Daromin 1 wells, measured and calculated values of reflectance differ significantly, showing VR_{eqv}VLR = 1.1%, 1.5% and 1.9%, respectively (Table 1). Such differences within a few kilometers are difficult to explain by differences in burial. Two explanations are possible, namely, separated pre-Emsian Małopolska Massif and Łysogóry Block thermal histories (Narkiewicz 2002) or elevated local-scale heat flow linked to the HCF. Based on recent data (Kozłowski et al. 2014), the second scenario seems the more likely, especially as detailed tectonics in the Daromin 1 borehole suggests its proximity to the HCF. Any certainty requires more data.

6.2. Organic maturity parameters and their use in determining Silurian source rock maturation

The thermal maturity of Silurian rocks in the HCM have been measured using independent methods such as vitrinite equivalent reflectance, Rock Eval, and organic molecular parameters. In most cases, the results correspond to those previously obtained both for older, Cambrian – Ordovician, and younger Devonian rocks (Belka 1990, Marynowski 1999, Narkiewicz et al. 2010), indicating increasing thermal maturity towards the HCF. It was possible to measure graptolite reflectance for the majority of samples, making this method universal and appropriate even for samples relatively poor in organic matter. Importantly, as hitherto presented data on vitrinite-like macerals in Paleozoic rocks were not converted into vitrinite reflectance values (Nehring-Lefeld et al. 1997; Swadowska, Sikorska 1998; Grotek 2006; Poprawa 2010), their comparison with actual vitrinite reflectance values measured for younger rocks seems questionable. In addition, all conclusions about hydrocarbon generation should be based on calculated reflectance results as differences between measured- and calculated reflectance values reach 0.3% (Table 1).

The T_{max} parameter was measured using Rock Eval, and also calculated from graptolite reflectance and organic parameters. Values correspond with those of thermal maturity shown by vitrinite equivalent reflectance. However, it is not recommended in the case of organic-poor or overmature samples. Thus, the use of the T_{max} parameter for the Silurian black shales is limited. Similar restrictions have been observed in other basins (e.g. Issler et al. 2012).

Molecular parameters such as MPI and MDR enable recalculation of values of vitrinite-reflectance parameters (Table 2). Despite the fact that MDR was used successfully by Marynowski (1999) for Devonian rocks, is not recommended here for the Silurian shales, because of their low contents of sulphur compounds; methyldibenzothiophenes were detected only in a few samples. Though values for MDR obtained seem to be realistic, the lack of sulphur compounds in the Silurian black shales limits their use. While phenantrene and methylphenanthrenes used for calculating the MPI ratio are very common in the shale samples, the parameter has not been endorsed for use for samples of II kerogen type (Radke 1988). The MPI seems to work better for less mature samples but is useless for samples of higher maturation (Table 2).

6.3. *Petroleum source-rock potential of lower Silurian shales in the Holy Cross Mountains*

Total organic-carbon contents in the shales studied fall between 0.24-7.85%. Only one sample does not exceed the threshold value of 0.5% defined by Peters and Cassa (1994). $S_1 + S_2$, used to evaluate hydrocarbon potential, varies from 0.25 mg HC/g TOC (Kleczanów well; 141 m) to 38.26 mg HC/g TOC (Zbrza PIG-1; 11.5 m). Four of the shale samples do not exceed a $S_1 + S_2$ value of 3 mg HC/g.

The petroleum potential of the Lower Silurian shales varies from poor to excellent. Those showing the highest potential are represented by the Zbrza PIG-1 (11.1-11.5 m) and Szumsko Kol.2 (20-22 m) samples (Fig. 3; Table 1). These results are in agreement with data presented by Malec et al. (2010). Our results also identified Llandovery black shales as significant potential source rocks for hydrocarbons. Moreover, as found by Malec et al. (2010), type II type kerogen predominates in Silurian shales (Fig. 4). However, in the Llandovery samples from Zbrza PIG-1 and Szumsko Kol.2 boreholes, organic matter thermal maturity seems to be to low for hydrocarbon generation or is on the first stage of generation (Table 1).

7. Conclusions

- The best tool for a maturation study of Silurian black shales in the Holy Cross Mountains appears to be the measurement of graptolite reflectance calculated as vitrinite equivalent reflectance.
- Based on a comparison of three different formulas used for the conversion of graptolite reflectance into vitrinite reflectance, we conclude that the equation most applicable to the Silurian shales in the HCM is that of Schmidt et al. (2015)
- Molecular parameters based on the distribution of *n*-alkanes, isoprenoids and methylphenanthrenes are of limited use in palaeotemperature reconstruction for Lower Palaeozoic sedimentary rocks
- Over the most of the HMC, the maturity of Lower Silurian black shales increases from S to N, reaching maximum values near the Holy Cross Fault. More data is needed to understand a more complicated pattern in the eastern part of the HCM.
- Rock Eval data confirm previous findings that Llandovery black shales are the Silurian source rocks most likely to generate hydrocarbons

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